

# Double-Quantum-Filtered NMR Signals in Inhomogeneous Magnetic Fields

A. Wiesmath, C. Filip,<sup>1</sup> D. E. Demco, and B. Blümich<sup>2</sup>

*Institut für Technische Chemie und Makromolekulare Chemie, Rheinisch-Westfälische Technische Hochschule, Worringerweg 1, D-52056 Aachen, Germany*

Received August 31, 2000; revised January 31, 2001; published online March 20, 2001

**The possibility of exciting and detecting proton NMR double-quantum coherences in inhomogeneous static and radiofrequency magnetic fields was investigated. For this purpose specialized pulse sequences which partially refocus the strongly inhomogeneous evolution of the spin system and generate double-quantum buildup and decay curves were implemented on the NMR MOUSE (mobile universal surface explorer). The theoretical justification of the method was developed for the simple two-spin- $\frac{1}{2}$  system. The performances of the same pulse sequences were also tested on a solid-state high-field NMR spectrometer. It was shown that DQ decay curves have a better signal-to-noise ratio in the initial time regime than DQ buildup curves. The double-quantum buildup and decay curves were recorded for a series of cross-linked natural rubber samples. These curves give access to quantitative values of the ratio of proton total residual dipolar couplings which are in good agreement with those measured in homogeneous fields. A linear dependence of these ratios on the sulfur-accelerator content was found.** © 2001 Academic Press

**Key Words:** double-quantum NMR coherences; NMR MOUSE; double-quantum buildup and decay curves; cross-linked natural rubber.

## INTRODUCTION

Multiple-quantum (MQ) coherences (1, 2), especially double (DQ)- and triple (TQ)-quantum coherences of  $^1\text{H}$  in dipolar-coupled systems, have been explored recently for the measurements of residual dipolar couplings and associated dynamic order parameters in elastomers like poly(styrene-co-butadiene) (3) and poly(isoprene) (4). It was shown that these couplings can be correlated with the cross-link density (3, 4) and the space distribution of strain (5). Parameter images can be recorded employing  $^1\text{H}$  DQ and TQ coherence filters in heterogeneous elastomers (5, 6). Moreover,  $^2\text{H}$  DQ-filtered NMR signals of deuterated poly(butadiene) oligomers incorporated into elastic rubber bands were used to generate contrast in  $^2\text{H}$  NMR images of local strain in stretched elastomers (7, 8). Further-

more, proton as well as deuterium DQ-filtered NMR imaging has been applied to map molecular order in biological tissues (9, 10). All of the above investigations have been performed using homogeneous static and radiofrequency (rf) magnetic fields and pulsed spatially constant field gradients.

Recently, a mobile NMR surface scanner (NMR MOUSE) has been developed for the nondestructive investigation of arbitrarily large objects (11, and references therein). The NMR MOUSE is characterized by strong inhomogeneities in the static and radiofrequency magnetic fields. Therefore, a detailed analysis of the spin system response to various pulse sequences is necessary in order to assess the measured NMR parameters (12). Furthermore, the possibility of recording  $^1\text{H}$  MQ-filtered NMR signals in these inhomogeneous fields has to be investigated in connection with the successful application of this method to elastomers (3–6) and biological tissues (9, 10).

The aim of this Communication is to show that proton DQ-filtered signals can be detected using an NMR MOUSE sensor operating in the presence of strongly inhomogeneous static and radiofrequency magnetic fields. The measurements were performed on the important class of materials of cross-linked elastomers. A new method is discussed theoretically and proved experimentally which allows for measuring DQ decay curves having as a starting point a maximum value of the excited DQ coherences. This procedure was also tested employing a solid-state superconducting NMR spectrometer using different pulse tilt angles which partially mimics the field inhomogeneities present for the NMR MOUSE. This method leads to an improved accuracy in the measurements of the ratio of the total residual dipolar couplings. The experiments were conducted on natural rubber samples with different cross-link densities, showing the sensitivity of the DQ buildup and decay curves to cross-link density. The possibility of measuring quantitatively the ratio of  $^1\text{H}$  total residual dipolar couplings from DQ decay curves recorded by the NMR MOUSE is also discussed.

## THEORY

The most simple method for exciting and detecting MQ coherences is based on time reversal procedures (cf. Fig. 1a) like

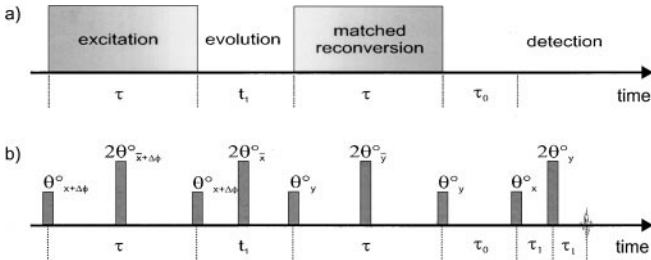
<sup>1</sup> On leave from the Institute for Isotopic and Molecular Technology, P.O. Box 700, RO 3400, Cluj-Napoca, Romania.

<sup>2</sup> To whom correspondence should be addressed.

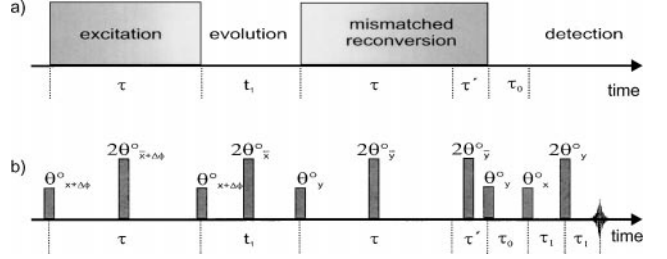
the nonselective three-pulse sequence (1, 2) or the variant presented in Fig. 1b. For the pulse sequence presented in Fig. 1 the duration of the excitation and reconversion periods is equal and the efficiency in pumping MQ coherences is increasing in the initial excitation/reconversion time regime (3, 4). A buildup curve is recorded in this case for which a maximum is present as a result of competitive effects of pumping MQ coherences and transverse relaxation of single-quantum coherences.

We shall consider in the following the spin system response to the *mismatched excitation/reconversion pulse sequence* (MERE) (see Fig. 2) used for excitation and detection of MQ coherences. The case of a two-spin- $\frac{1}{2}$  system will be treated in the presence of homogeneous magnetic fields for which well-defined arbitrary pulse flip angles can be defined all over the sample volume. This will make it possible for us to understand how the MERE pulse sequence works for NMR MOUSE, i.e., in strongly inhomogeneous magnetic fields where a distribution of pulse flip angles exists. Nevertheless, the radiofrequency pulse phases are the same for each sample voxel. The new feature of this pulse sequence is related to the possibility of generating MQ coherence decay curves which can be adjusted to begin with a maximum MQ signal. This will allow for a more accurate determination of the residual dipolar couplings compared with the method employing MQ buildup curves (cf. Fig. 1).

The spin system response for an isolated two-spin- $\frac{1}{2}$  system can be described by an equivalent quadrupolar nucleus with spin  $I = 1$  (4, 13). Under the action of the pulse sequence presented in Fig. 1b the reduced density operator  $\sigma$  can be conveniently described in terms of irreducible tensor operators  $T_{k,l}$  (1) at various time points. The effect of partially refocusing  $2\theta$  rf pulses (cf. Fig. 2b) is neglected because it is not essential for the filtration of DQ coherences. The experiment starts with a spin system having a  $z$  polarization, i.e.,  $\sigma(0^-) \propto T_{1,0}$ . After the action of



**FIG. 1.** (a) Schematic representation of the experiment for matched excitation and reconversion of MQ coherences used for recording buildup curves. This scheme is similar to a two-dimensional MQ experiment but it is used with fixed evolution time  $t_1$  and variable, but equal, excitation/reconversion times  $\tau$ . (b) A five-pulse sequence with an arbitrary flip angle  $\theta$ , supplemented by  $2\theta$  partially refocusing pulses for measuring DQ-filtered coherences with matched, variable excitation/reconversion times. The evolution time  $t_1$  is kept short and constant and a  $2\theta$  pulse is applied at the middle of this interval for partially refocusing the DQ coherences evolution under inhomogeneous Hamiltonians.



**FIG. 2.** (a) Schematic representation of the experiment for mismatched excitation and reconversion of MQ coherences used for recording decay curves. The excitation time  $\tau$  and the evolution time  $t_1$  are kept fix and only the mismatched reconversion time  $\tau'$  is varied. The parameter  $\tau$  is set to the maximum of the DQ buildup curves. (b) A five-pulse sequence with an arbitrary flip angle  $\theta$ , supplemented by  $2\theta$  partially refocusing pulses for measuring DQ-filtered coherence decay curves. The evolution time  $t_1$  is kept short and constant and a  $2\theta$  pulse is applied at the middle of this interval for partially refocusing the coherence evolution under inhomogeneous Hamiltonians.

the first hard  $\theta$  pulse we can write

$$\sigma(0^+) \propto T_{1,0} \cos \theta + iT_{1,1}(s) \sin \theta, \quad [1]$$

where  $T_{1,1}(s)$  is the symmetric irreducible tensor operator of  $T_{1,\pm 1}$ .

The free evolution under the effect of the truncated residual dipolar Hamiltonian  $\bar{H}_d^{(0)} = \bar{\omega}_d T_{2,0}$ , where  $\bar{\omega}_d$  is the preaveraged intra- and intergroup dipolar coupling constant (4, and references therein), leads to the density operator

$$\begin{aligned} \sigma(\tau^-) \propto & T_{1,0} \cos \theta + iT_{1,1}(s) \cos \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) \sin \theta \\ & + \sqrt{2} T_{2,1}(a) \sin \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) \cos \theta. \end{aligned} \quad [2]$$

After the action of the second rf  $\theta$  pulse, i.e., at the end of the excitation period for dipolar-encoded longitudinal magnetization ( $T_{1,0}$ ), in-phase single-quantum ( $T_{1,1}(s)$ ), antiphase single-quantum ( $T_{2,1}(a)$ ) (which denotes the antisymmetric combination of  $T_{2,\pm 1}$ ), and double-quantum coherences ( $T_{2,\pm 2}$ ) have been excited. The part of the density operator describing DQ coherences is given by

$$\sigma(\tau^+) \propto T_{2,2}(a) \sin \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) \sin^2 \theta. \quad [3]$$

The DQ-encoded  $z$  polarization at the end of the reconversion period and the  $z$  filter of duration  $\tau_0$  (cf. Fig. 2b) can be evaluated as above, and finally the DQ-filtered signal is given by

$$S_{DQ}(\tau') \propto \left\langle \sin \left( \sqrt{\frac{3}{2}} \bar{\omega}_D (\tau + \tau') \right) \sin \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) \right\rangle \sin^4 \theta,$$

where the evolution of DQ coherences during the  $t_1$  period has been neglected. The symbol  $\langle(\cdot\cdot\cdot)\rangle$  represents the averages taken over the orientation of the spin-pair internuclear vectors and the statistics of the end-to-end vector (3, 4). In the case of the NMR MOUSE Eq. [4] describes the signal originating from a particular sample voxel characterized by an rf pulse having a  $\theta$  flip angle. In the presence of transverse relaxation of single-quantum coherences during excitation and reconversion periods Eq. [4] has to be multiplied by the function  $\exp[-(2\tau + \tau')/T_{2,eff}]$ , where  $T_{2,eff}$  is the effective transverse relaxation time. For an rf pulse flip angle of  $\theta = 90^\circ$  and matched excitation/reconversion pulse sequence, i.e.,  $\tau' = 0$ , Eq. [4] becomes identical with the DQ signal derived for a static collection of spin- $\frac{1}{2}$  pairs (4). If the  $\tau'$  interval fulfills the conditions  $\omega_D\tau' \ll 1$  and  $\tau' \ll T_{2,eff}$  we can write following Eq. [4]

$$S_{DQ}(\tau') \propto \left\langle \sin^2 \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) \left( 1 - \frac{3}{4} \bar{\omega}_D^2 \tau^2 \right) \right\rangle \times \exp[-2\tau/T_{2,eff}] \sin^4 \theta. \quad [5]$$

The above equation is derived from Eq. [4] for a  $\tau$  parameter which has a value in the region of the maximum of the DQ buildup curve, i.e., for  $\langle \sin^2(\sqrt{\frac{3}{2}} \bar{\omega}_D \tau) \rangle \approx 1$  and  $\langle \cos(\sqrt{\frac{3}{2}} \bar{\omega}_D \tau) \rangle \approx 0$ . If these conditions are fulfilled we can approximate Eq. [5] by

$$S_{DQ}(\tau') \propto \left( 1 - \frac{3}{4} \langle \bar{\omega}_D^2 \rangle \tau^2 \right) \exp[-2\tau/T_{2,eff}] \sin^4 \theta. \quad [6]$$

We note that this approximation is not necessary for the evaluation of DQ buildup curves (4). Nevertheless, the values of the residual dipolar couplings measured by the DQ buildup and decay curves are in good agreement as is shown below. This shows that the approximation involved in deriving Eq. [6] is valid. Finally, the normalized DQ-filtered signal is given by

$$\frac{S_{DQ}(\tau')}{S_{DQ}(0)} \propto \left( 1 - \frac{3}{4} \langle \bar{\omega}_D^2 \rangle \tau^2 \right) \sin^4 \theta; \quad [7]$$

i.e., the signal represents a DQ decay curve starting from an initial time  $\tau' = 0$ , after DQ coherence pumping for a duration  $\tau$ . The slope of the DQ decay curve with regard to  $\tau^2$  gives a quantity related to the total residual dipolar coupling of the elastomer segments. The sensitivity to the residual dipolar couplings can be defined as a derivative of the curve slope versus  $\langle \bar{\omega}_D^2 \rangle$ . For the DQ decay curves this derivative is 3/4, being two times lower than that for the DQ buildup curves.

For a multispin dipolar topology the effect of pumping DQ high-order spin correlations and multiple-quantum coherences leads to a more complex treatment than that described above. Nevertheless, Eq. [7] is expected to be still valid in the limit of small values of  $\tau'^2$ .

## EXPERIMENTAL

### Samples

The elastomer system investigated is based on commercially available natural rubber SMR10 (Malaysia). As additives, the samples of the cross-linking series contain 3 phr (parts per hundred rubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents of the different samples are shown in Table 1. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-*tert*-butyl-sulfenamide). After the compounds were mixed in a laboratory mixer at 50°C, the vulcanization was performed at 160°C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low-frequency shear modulus at a temperature of 160°C in the vulcameter directly after the vulcanization. The measurements were performed with an oscillation amplitude of  $\pm 0.50^\circ$  and a frequency of 1.67 Hz.

### NMR Experiments

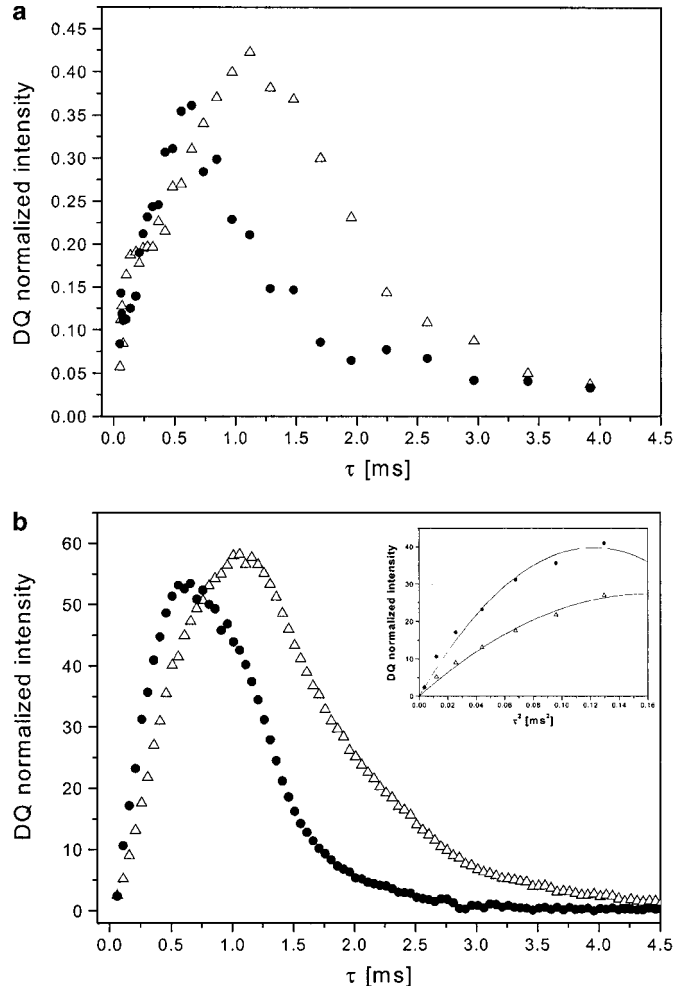
The  $^1\text{H}$  NMR experiments in inhomogeneous fields were performed on a homemade NMR MOUSE sensor equipped with a Bruker Minispec spectrometer operating at a carrier frequency of 20.1 MHz. The coil geometry resulted in a sensitive volume of about  $9 \times 4$  mm in plane and 0.5 mm in depth. Further details are published in Ref. (14). The rf pulse length employed in all of the measurements had a value of 2.5  $\mu\text{s}$ , the evolution time was  $t_1 = 60 \mu\text{s}$ , the  $z$ -filter time was  $\tau_0 = 500 \mu\text{s}$ , and Hahn echo time was  $\tau_1 = 100 \mu\text{s}$  (cf. Figs. 1b and 2b). The DQ decay curves were recorded with fixed values of  $\tau = 1.05$  and 0.75 ms (cf. Fig. 2b) corresponding to the maximum of the DQ buildup curves for the natural rubber samples NR1 and NR5, respectively. The NMR experiments in the homogeneous field were performed at a  $^1\text{H}$  frequency of 500.045 MHz on a Bruker DSX 500 spectrometer. The  $90^\circ$  pulse length was 2  $\mu\text{s}$ . To partially mimic the effect of rf pulse inhomogeneity the DQ-filtered signals were recorded with a rf pulse flip angle of about  $\theta = 60^\circ$ . The pulse delays were the same as those used for the measurements performed with the NMR MOUSE. The acquisition was performed without employing a Hahn echo. Two partially refocusing  $2\theta$  pulses were applied in the middle of the  $\tau$  and  $\tau'$  periods of the mismatched reconversion period (cf. Fig. 2b). Phase cycling of the DQ coherence filtration schemes (1, 2) was applied in all experiments.

**TABLE 1**  
**Cross-Link Series of Natural Rubber**

Sample	Sulfur-accelerator content (phr)
NR1	1-1
NR2	2-2
NR3	3-3
NR4	4-4
NR5	5-5

## RESULTS

The possibility of exciting  $^1\text{H}$  DQ-filtered signals using the NMR MOUSE and the pulse sequence presented in Fig. 1b is proved by the DQ buildup curves in Fig. 3a recorded on the natural rubber samples NR1 and NR5 (cf. Table 1). In the initial pumping regime the slopes of the DQ buildup curves are different, reflecting different values of the residual dipolar couplings. The signal-to-noise ratio is relatively low, making the quantitative evaluation of residual dipolar couplings inaccurate. A better



**FIG. 3.**  $^1\text{H}$ -normalized DQ buildup curves for the natural rubber samples NR1 ( $\Delta$ ) and NR5 ( $\bullet$ ) with different cross-link densities (cf. Table 1). The buildup curves have been recorded using the pulse sequence of Fig. 1b. (a) The DQ-filtered signal dependence on excitation and reconversion times  $\tau$  recorded using the NMR MOUSE. The DQ signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for the buildup curves. (b) The normalized DQ buildup curves recorded with the Bruker DSX 500 NMR spectrometer. The pulse sequence of Fig. 1b was used with a pulse flip angle of about  $\theta = 60^\circ$  and pulse delays identical to those used in the measurements with the NMR MOUSE. The inset shows the dependence on  $\tau^2$  for the buildup curves in the initial excitation regime. The solid lines represent the best fit of the data with a polynomial function of order 6 in  $\tau$ .

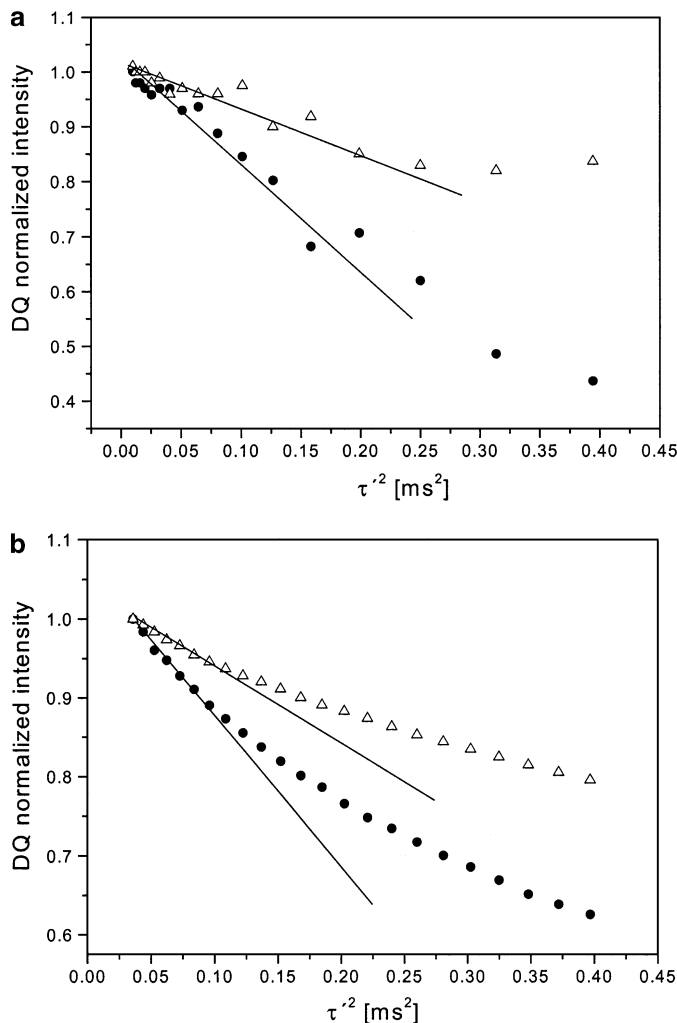
sensitivity to the cross-link density is given by the times at which DQ buildup curves reach the maximum values. This is due to the combined effect of the increasing efficiency of pumping DQ coherences with increasing excitation/reconversion times in the initial pumping regime and transverse relaxation of the single-quantum coherences (3, 4). Both quantities are affected by the cross-link density. For multispin dipolar networks higher-order multiple-quantum coherences and spin correlations will also be excited and contribute to the decrease of the DQ signal amplitudes. In order to test the efficiency of the phase cycling scheme used for filtering DQ coherences and to partially mimic the distribution of rf pulse flip angles the  $^1\text{H}$  DQ buildup curves of NR1 and NR5 have been recorded on a Bruker DSX 500 solid-state NMR spectrometer using the pulse sequence presented in Fig. 1b with  $\theta = 60^\circ$  (cf. Fig. 3b). The data obtained on the DSX 500 and on the NMR MOUSE show good agreement. The inset of Fig. 3b shows the evolution of the DQ-filtered signal intensities in the initial excitation time regime versus  $\tau^2$ . The lines represent the best fit of the data with a polynomial function of order 6 in  $\tau$ . The coefficient of the  $\tau^2$  term is related to  $\langle \bar{\omega}_D^2 \rangle$  (3, 4). We can note here that the DQ buildup curves in the regime of long excitation times could be slightly different for the measurements performed with the NMR MOUSE and high-field NMR spectrometers as a result of a possible dependence of the transverse relaxation rate on the magnetic field strength. Nevertheless, this effect was not observed for the investigated cross-link natural rubber series. The maximum of the DQ buildup curves recorded at about 20 and 500 MHz is reached for the same  $\tau$  values (cf. Fig. 3a and Fig. 3b).

In order to improve the signal-to-noise ratio for the DQ-filtered signals a new procedure was introduced based on the MERE pulse sequence (cf. Fig. 2b). The  $^1\text{H}$ -normalized DQ decay curves measured using the NMR MOUSE and the Bruker DSX 500 spectrometer for the natural rubber samples NR1 and NR5 which differ in cross-link density (cf. Table 1) are presented in Figs. 4a and 4b, respectively. The ratio of the slopes for the fitted straight lines in  $\tau^2$  involves the  $\langle \bar{\omega}_D^2 \rangle$  term (see Eq. [7]) for the two natural rubber samples NR5 and NR1. This ratio (see below) is in good agreement (about 10%) with that obtained from the measurements performed with the NMR MOUSE.

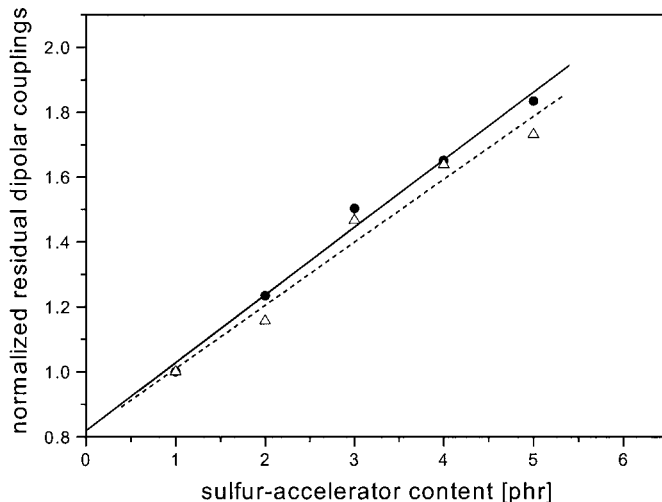
To justify the approximations used for the derivation of Eq. [7] a comparison between the  $\langle \bar{\omega}_D^2 \rangle$  values measured from DQ buildup and decay curves was made. For this purpose the data recorded with the Bruker DSX 500 spectrometer shown in Figs. 3b (see inset) and 4b were used. For the natural rubber samples NR1 and NR5 we get the ratios  $\langle \bar{\omega}_D^2 \rangle_{NR5}^{DQ\text{ buildup}} / \langle \bar{\omega}_D^2 \rangle_{NR1}^{DQ\text{ buildup}} \cong 2.5$  from the data presented in the inset of the Fig. 3b, and  $\langle \bar{\omega}_D^2 \rangle_{NR5}^{DQ\text{ decay}} / \langle \bar{\omega}_D^2 \rangle_{NR1}^{DQ\text{ decay}} \cong 3$  from the data shown in Fig. 4b. In the limit of the experimental errors these ratios are in good agreement, thus showing that the approximations involved in the derivation of Eq. [7] are justified.

In order to investigate the possibility of using the NMR MOUSE sensor to measure the ratio of the total (intragroup as

well as intergroup) residual dipolar couplings of two samples, with one sample used as a reference,  $^1\text{H}$  DQ decay curves have been recorded for the natural rubber cross-link series of Table 1. The initial decay time regime  $\tau'$  was exploited to evaluate the values of the square of the total residual dipolar coupling given by  $\langle\bar{\omega}_D^2\rangle$  (cf. Eq. [7]). The measurements were performed on an NMR MOUSE and a Bruker DSX 500 spectrometer using the  $\tau$  values (cf. Fig. 2b) corresponding to the maximum of DQ buildup curves for each sample in the cross-linked series. The residual dipolar couplings ratios  $\langle\bar{\omega}_{d,NRi}^2\rangle^{1/2}/\langle\bar{\omega}_{d,NR1}^2\rangle^{1/2}$  for different natural rubber samples labeled by indices  $i = 1, 2, 3, 4,$



**FIG. 4.**  $^1\text{H}$ -normalized DQ decay curves for the natural rubber samples NR1 ( $\Delta$ ) and NR5 ( $\bullet$ ) (cf. Table 1). The DQ decay curves have been recorded using the MERE pulse sequence of Fig. 2b. (a) The DQ-filtered signal recorded using the NMR MOUSE versus  $\tau'^2$ , where  $\tau'$  is the mismatched reconversion time. (b) The normalized DQ decay curves recorded with the Bruker DSX 500 NMR spectrometer versus  $\tau'^2$ . The pulse sequence of Fig. 2b was used with a pulse flip angle of about  $\theta = 60^\circ$  and pulse delays identical to those used in the measurements with the NMR MOUSE. The DQ signals were normalized to the maximum intensity of the DQ buildup curves. The solid lines represent the best fit of the experimental data in the initial  $\tau'^2$  regime of mismatched reconversion.



**FIG. 5.** The normalized values of the residual dipolar couplings  $\langle\bar{\omega}_{d,NRi}^2\rangle^{1/2}/\langle\bar{\omega}_{d,NR1}^2\rangle^{1/2}$  for the cross-linked natural rubber series of Table 1 versus sulfur-accelerator content. These quantities are determined by measuring the slopes of the DQ decay curves represented versus  $\tau'^2$  (cf. Fig. 4). The ratios  $\langle\bar{\omega}_{d,NRi}^2\rangle^{1/2}/\langle\bar{\omega}_{d,NR1}^2\rangle^{1/2}$  for  $i = 2, 3, 4,$  and  $5$  are obtained from the data recorded using the NMR MOUSE ( $\bullet$ ) and the Bruker DSX 500 spectrometer ( $\Delta$ ) employing the MERE pulse sequence (cf. Fig. 2b). The continuous and dashed lines represent the best fit of the  $\langle\bar{\omega}_{d,NRi}^2\rangle^{1/2}/\langle\bar{\omega}_{d,NR1}^2\rangle^{1/2}$  ratios measured with the NMR MOUSE and the DSX 500 spectrometer, respectively.

and 5 (see Table 1) are shown in Fig. 5 versus sulfur-accelerator content in phr. In the limit of experimental errors these ratios show a linear dependence. This linear dependence underlines again the validity of the simple model employed for evaluating residual dipolar couplings (15) which has been used previously in studies of polybutadiene (3, 16, 17) and synthetic 1,4-*cis*-polyisoprene (4). However, the lines in Fig. 5 do not cross the origin but provide a finite value for residual dipolar couplings for un-cross-linked natural rubber. As noted before (15) this is not in contradiction with the applied model, but reflects the influence of the local chain order (physical cross-links). It is evident from Fig. 5 that over the range of cross-link densities that has been examined, there is about an 80% increase in the normalized value of the residual dipolar couplings. The residual dipolar couplings measured in homogeneous and inhomogeneous magnetic fields differ by about 10%, proving that the NMR MOUSE can provide quantitative values for relative  $^1\text{H}$  total residual dipolar couplings for elastomers.

We have also found that the broadband eight-pulse sequence (2) was not efficient in pumping DQ coherences, probably as a result of increased volume selection produced by multiple rf pulses with the NMR MOUSE (12).

## CONCLUSIONS

The possibility of detecting  $^1\text{H}$  DQ-filtered NMR signals in cross-linked elastomers using an NMR MOUSE sensor was demonstrated. To investigate the effects of the field

inhomogeneities on the DQ buildup and decay curves the methods employed were tested on a solid-state Bruker DSX 500 NMR spectrometer for an arbitrary value of the pulse tip angle. The DQ buildup and decay curves in the initial time regimes are not affected by the magnetic field inhomogeneity because the filtration of these coherences is achieved by the phase cycling procedure. In inhomogeneous fields only the phases of radiofrequency pulses are the same for all the voxels in the sample. Radiofrequency pulse flip angles are widely distributed. Because only the rf pulse delays are modified in these experiments and not the number of pulses, the artifacts induced by volume selection are not present like in the case of measurements made with Carr–Purcell pulse sequences (12).

The newly introduced method of DQ decay curves is characterized by an improved accuracy in measuring the ratio of the residual dipolar couplings as a result of better signal-to-noise ratio as compared to the DQ buildup curves. Nevertheless, for optimum setting of this method, the DQ buildup curve has to be recorded first. Moreover, DQ decay curves are less sensitive to the changes in the value of the residual dipolar couplings as compared to the DQ buildup curves. It was also shown that samples having different values of the total residual dipolar couplings in a cross-linked elastomer series can be compared quantitatively using the NMR MOUSE. The method of the DQ decay curves can be also applied in the case of experiments done in homogeneous magnetic fields or under magic-angle sample spinning for measuring chemically site selective dynamic order parameters (3). Moreover, this procedure can be used for  $^1\text{H}$  NMR contrast filters to record parameter images of residual dipolar couplings in elastomers having better spatial resolution compared with that based on DQ buildup coherences (5, 6).

The possibility of recording proton DQ-filtered NMR signals will make the use of the NMR MOUSE more promising for the characterization of ordered tissues like intervertebral disk, connective tissues, muscles, and blood vessels. The excitation of other spin modes like dipolar-encoded longitudinal magnetization and dipolar order using the NMR MOUSE as well as extending the sphere of applications of these procedures is currently under study.

### ACKNOWLEDGMENTS

This work was supported by grants from the Deutsche Forschungsgemeinschaft (Forschegruppe BL-231/23-1) and by the German Aerospace Center (DLR), and Bundesministerium für Bildung und Forschung (BMBF) under German–Israeli Project Cooperation (DIP). The authors are also grateful to Dr. K. Unseld and V. Hermann, Dunlop GmbH, Hanau, for providing the samples and helpful information. The authors acknowledge stimulating discussion

with Professor Gil Navon, Dr. Uzi Eliav, Dr. Ute Görke, Dr. Siegfried Stapf, and Dr. Marko Bertmer. C.F. thanks Deutsche Forschungsgemeinschaft for a visiting scientist grant.

### REFERENCES

1. R. R. Ernst, G. Bodenhausen, and A. Wokaun, "Principles of Nuclear Magnetic Resonance in One and Two Dimensions," Clarendon, Oxford (1987).
2. M. Munowitz and A. Pines, Principles and applications of multiple-quantum NMR, *Adv. Chem. Phys.* **66**, 1–152 (1987).
3. R. Graf, D. E. Demco, S. Hafner, and H. W. Spiess, Selective residual dipolar couplings in cross-linked elastomers by  $^1\text{H}$  double-quantum NMR spectroscopy, *Solid State Nucl. Magn. Reson.* **12**, 139–152 (1998).
4. M. Schneider, L. Gasper, D. E. Demco, and B. Blümich, Residual dipolar couplings by  $^1\text{H}$  dipolar encoded longitudinal magnetization, double- and triple-quantum nuclear magnetic resonance in cross-linked elastomers, *J. Chem. Phys.* **111**, 402–415 (1999).
5. M. Schneider, D. E. Demco, and B. Blümich, NMR imaging of proton residual dipolar coupling from strained elastomers, submitted for publication.
6. M. Schneider, D. E. Demco, and B. Blümich,  $^1\text{H}$  NMR imaging of residual dipolar couplings in cross-linked elastomers: Dipolar-encoded longitudinal magnetization, double-quantum, and triple-quantum filters, *J. Magn. Reson.* **140**, 432–441 (1999).
7. M. Klinkenberg, P. Blümmler, and B. Blümich,  $^2\text{H}$ -NMR imaging of stress in strained elastomers, *Macromolecules* **30**, 1038–1043 (1997).
8. M. Klinkenberg, P. Blümmler, and B. Blümich,  $^2\text{H}$  NMR imaging of strained elastomers, *J. Magn. Reson. A* **119**, 197–203 (1996).
9. L. Tsoref, H. Shinar, Y. Seo, U. Eliav, and G. Navon, Proton double-quantum filtered MRI—A new method for imaging ordered tissue, *Magn. Reson. Med.* **40**, 720–726 (1998).
10. U. Eliav and G. Navon, A study of dipolar interactions and dynamic processes of water molecules in tendon by  $^1\text{H}$  and  $^2\text{H}$  homonuclear and heteronuclear multiple-quantum-filtered NMR spectroscopy, *J. Magn. Reson.* **137**, 295–310 (1999).
11. B. Blümich, "NMR Imaging of Materials," Clarendon Press, Oxford (2000).
12. F. Balibanu, K. Hailu, R. Eymael, D. E. Demco, and B. Blümich, Nuclear magnetic resonance in inhomogeneous magnetic fields, *J. Magn. Reson.* **145**, 246–258 (2000).
13. J. Gottwald, D. E. Demco, R. Graf, and H. W. Spiess, High-resolution double-quantum NMR spectroscopy of homonuclear spin pairs and proton connectivities in solids, *Chem. Phys. Lett.* **243**, 314–323 (1995).
14. G. Eidmann, R. Savelsberg, P. Blümmler, and B. Blümich, The NMR MOUSE, a mobile universal surface explorer, *J. Magn. Reson. A* **122**, 104–109 (1996).
15. P. Sotta, C. Fülber, D. E. Demco, B. Blümich, and H. W. Spiess, Effect of residual dipolar interactions on the NMR relaxation in cross-link elastomers, *Macromolecules* **29**, 6222–6230 (1996).
16. D. E. Demco, S. Hafner, C. Fülber, R. Graf, and H. W. Spiess, Two-dimensional magnetization-exchange NMR spectroscopy in cross-linked elastomers, *J. Chem. Phys.* **105**, 11285–11296 (1999).
17. L. Gasper, D. E. Demco, and B. Blümich, Proton residual dipolar couplings by NMR magnetization-exchange in cross-linked elastomers: Determination and imaging, *Solid State Nucl. Magn. Reson.* **14**, 105–116 (1999).